Original Article
http://doi.org/10.17072/2223-1838-2025-1-17-32

Tungsten (VI) Complexes with 2-Hydroxy-5-chlorthiophenol in the Presence of Aminophenols and Their Application

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Abstract. In the present paper, we report results from liquid-liquid extraction-spectrophotometric experiments on two different systems, each of which containing tungsten (VI), a 2-hydroxy-5-chlorothiophenol (H_2L), and 2-(N,N-dimethylaminomethyl)-4-chlorphenol (AP_1) or 2-(N,N-dimethylaminomethyl)-4-bromphenol (AP_2). In the complex formation with H_2L, tungsten (VI) is reduced to tungsten (V) by the reagent itself. This fact was also confirmed by ESR spectrometry. Extraction of mixed ligand complexes is maximal at pH 4,1–5,2. The absorption maxima of the mixed-ligand complex (MLC) W(V)–L–$AP^{1,2}$ lie in the range of 476–480 nm. Molar coefficients of absorption make (2,0–2,8)$\cdot 10^4$. The optimum amount of AP for the maximum binding of the anionic hydroxyl thiophenolate complex of tungsten [W(V)–L] into an ionic associate was determined by varying the quantity of AP added. For the formation of MLC W(V)–L–$AP^{1,2}$, the concentration of $1{,}2\cdot 10^{-3}$ mol/l of H_2L and $2{,}0\cdot 10^{-3}$ mol/l of $AP^{1,2}$ in the solution is required. MLC of W(V)–L–$AP^{1,2}$ were stable in aqueous and organic solvents and did not decompose for three days, and after extraction, more than a month. The maximum absorbance is reached within 5–8 minutes. Beer's law is obeyed over the concentration range 0,10–18 µg W(V)/ml. The method is free from common interferences. The proposed method were applied to the determination of tungsten in steel and samples of soil.

Keywords: tungsten, 2-hydroxy-5-chlorothiophenol, aminophenols, ligand, chloroform

For citation: Zalov, A.Z., Shirinov, E.G. and Safarova, P.S. (2025) Tungsten (VI) Complexes with 2-Hydroxy-5-chlorthiophenol in the Presence of Aminophenols and Their Application, *Bulletin of Perm University. Chemistry*, vol. 15, no. 1, pp. 17–32. http://doi.org/10.17072/2223-1838-2025-1-17-32

Научная статья
УДК 543.48
http://doi.org/10.17072/2223-1838-2025-1-17-32

Комплексы вольфрама (VI) с 2-гидрокси-5-хлортиофенолом в присутствии аминофенолов и их применение

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Аннотация. В статье сообщается о результатах экспериментов по экстракционно-спектрофотометрическому анализу двух систем системах, содержащих вольфрам (VI), 2-гидрокси-5-хлортиофенол (H_2L) и 2-(N,N-диметиламинометил)-4-хлорфенол (AP^1) или 2-(N,N-диметиламинометил)-4-бромфенол (AP^2). При комплексообразовании с H_2L вольфрам (VI) восстанавливается до вольфрама (V) самим реагентом. Этот факт подтвержден методом ЭПР-спектрометрии. Экстракция смешанно-лигандных комплексов максимальна при pH 4,1–5,2. Максимумы поглощения смешанно-лигандного комплекса W(V)–L–AP1,2 лежат в диапазоне 476–480 нм. Молярные коэффициенты поглощения составляют (2,0–2,8)$\cdot 10^4$. Оптимальное количество AP для максимального связывания анионного гидроксильного тиофенолятного комплекса вольфрама [W(V)–L] в ионный ассоциат определялось путем варьирования количества добавленного AP. Для образования комплекса W(V)–L–$АП^{1,2}$ требуется концентрация $1{,}2\cdot 10^{-3}$ моль/л H_2L и $2{,}0\cdot 10^{-3}$ моль/л $AP^{1,2}$ в растворе. Комплексные соединения W(V)–L–$AP^{1,2}$ стабильны в водных и органических растворителях и не разлагаются в течение трех суток, а после экстракции – более месяца. Максимальное поглощение достигается в течение 5–8 мин. Закон Бера соблюдается в диапазоне концентраций 0,10–18 мкг W(V)/мл. Метод свободен от общих помех. Предложенный метод был применен для определения вольфрама в стали и образцах почвы.

Ключевые слова: вольфрам, 2-гидрокси-5-хлортиофенол, аминофенолы, лиганд, хлороформ

Для цитирования: Залов А.З., Ширинов Э.Г., Сафарова П.С. Комплексы вольфрама (VI) с 2-гидрокси-5-хлортиофенолом в присутствии аминофенолов и их применение // Вестник Пермского университета. Серия «Химия». 2025. Т. 15, № 1. С. 17–32. http://doi.org/10.17072/2223-1838-2025-1-17-32

Determination of trace metal ions is very important in the context of environmental protection, food and agricultural chemistry and high purity materials, and also for monitoring environmental pollution. Several sensitive methods have been developed for the determination of metal ions. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment required. However, direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences [1]. Preconcentration and separation methods have been routinely used to eliminate matrix effects and cope with low metal levels [2].

Currently, the widely used techniques for preconcentration and separation of trace metals include liquid–liquid extraction [3, 4], ion-exchange [5, 6], coprecipitation [7–8], solid-phase extraction [10–15], flotation [16], electrochemical deposition [17], and cloud point extraction [18].

Spectrophotometric methods [19–23] are among the most precise instrumental methods of analysis for the determination of elements in trace amounts. These methods are remarkable for their versatility, sensitivity and precision. In these methods, a very extensive range of concentrations may be covered for the trace analysis of the elements.

The direct determination of tungsten in various matrices such as geological samples, steels, natural waters, etc. has presented some problems, due to the low tungsten content and large concentration of accompanying elements. Many preconcentration and separation methods have been used for the determination of tungsten at low concentrations, such as liquid-liquid extraction [19, 20], adsorption [21] and ion exchange [22, 23].

There are various spectrophotometric methods which suffer from low sensitivity, non-selectivity and complexity in the procedures for the determination of tungsten in trace amounts using thiocyanate, vanadophosphoric acid as ligands [24]. Many organic reagents have been used as analytical reagents for spectrophotometric determination of tungsten but most of these are not suitable for routine analysis of the metal ion due to one or more of the above drawbacks [19, 21, 24].

This prompted us to search for new and more advanced methods and accordingly we synthesized a very effective reagent 2-hydroxy-5-chlorothiophenol (H_2L), which was used as a complexing agent for spectrophotometric determination of metal ions in order to meet the above requirements [25–35].

In the present paper, we report results from liquid-liquid extraction-spectrophotometric experiments on 2 different systems, each of which containing W(VI), a H_2L and an aminophenols ($AP^{1,2}$) (as aminophenole 2-(N,N-dimethyl-aminomethyl)-4-chlorphenol (AP^1) and 2-(N,N-dimethyl-aminomethyl)-4-bromphenol (AP^2) were used).

The procedure has been applied satisfactorily to the determination of tungsten in soils and plants samples.

Experımental

Reagents and solutions. A standard stock solution (100 mL) of tungsten (VI) containing 1 mg ml^{-1} of the metal ion is prepared by dissolving an accurately weighed amount (0,179 g) of sodium tungstate in distilled water. The concentration of the tungsten solution was adjusted gravimetrically by sedimenting tungsten in the form of H_2WO_4 and weighing WO_3 [21, 24]. Lower concentrations at μg/ml (10, 20, 50 and 100) level are prepared by suitable dilution there from.

Chloroform was purified by washing with conc. H_2SO_4 and shaking with distilled water followed by washing with a 5% solution of NaOH. Chloroform is used for extraction of W(VI)–L–AP^{1,2} complex. H_2L is prepared by reported methods [36] as follows.

An optimum acidity was created by means of 0,01 mol/l HCl or an ammonium acetate buffer solution.

Instrumentation. The optical density of the extract was measured on a KFK-2 and SF-26 with a cuvette thickness of 0,5 and 1,0 cm, respectively. The pH of the solution was measured on an I-120.2 device. IR spectra were recorded on a Bruker spectrophotometer. L was analyzed on a Shimadzu LC-10AD liquid chromatograph and a PE SCIEX API 150EX mass spectrometer. The purity of the compounds obtained was controlled by TLC.

Procedure. Portions of a working tungsten solution, 0,1 to 0,8 ml with an increment of 0,1 ml, 1,0–2,0 ml of 0,01 mol/l HCl, and 0,3–0,5 ml of a 0,01 mol/l H_2L solution were placed in calibrated test tubes with ground stoppers. The mixture was stirred thoroughly for 5 min to reduce tungsten, and 2,0–3,0 ml of a 0,01 mol/l solution of AP^{1,2} was added. The volume of the organic phase was adjusted to 5 ml with chloroform, and the volume of the aqueous phase was brought to 20 ml with distilled water. After the formation of the hydroxythiophenolate complex of tungsten, it was extracted, and the absorbance of extracts was measured by a KFK-2 photoelectrocolorimeter at 490 nm.

2-hydroxy-5-chlorothiophenol [36]. Yield 89 %. IR spectrum, ν, cm^{-1}:1580 (C_6H_5), 2570 (SH), 3460 (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5,70 (s, $1H_{OH}$), 3,40 (s, $1H_{SH}$), d.d. 7,05 (s, H_{Ar}), 6,25 m (s, $2H_{Ar}$). Found, %: C 43,79; H 3,64; O 9,17; S 19,15; Cl 22,08. C_6H_5OSCl. Calculated, %: C 44,85; H 3,11; O 9,97; S 19,94; Cl 22,12. UV spectrum ($CHCl_3$), λ_{max}, nm: 283.

General procedure for the synthesis of complexes 1 and 2. W(V) complexes were obtained by the exchange reaction between tungsten (V) salt L and AP^{1,2}. For this purpose, the prepared solution of L and Am^{1,2} in ethanol was added to 10 ml of an ethanol solution of the salt $Na_2WO_4 \cdot 2H_2O$ (0,145 g, 672 mmol). The solution was stirred at 60°C for 25 min. After 1 day, dark red crystals began to precipitate. The crystals were filtered, washed with ethanol and dried in a desiccator under vacuum to constant weight. The yields were 0,029 g for 1 and 0,034 g for 2.

Extractant selection. For the extraction of complexes, we used $CHCl_3$, $C_2H_4Cl_2$, CCl_4, C_6H_6, C_6H_5-CH_3, C_6H_5Cl, *iso*-C_4H_9OH, *iso*-$C_5H_{11}OH$, *n*-C_4H_9OH and their mixes. Extractability of complexes was estimated in coefficient of distribution (*D*) and extent of extraction (R%) [20, 21]:

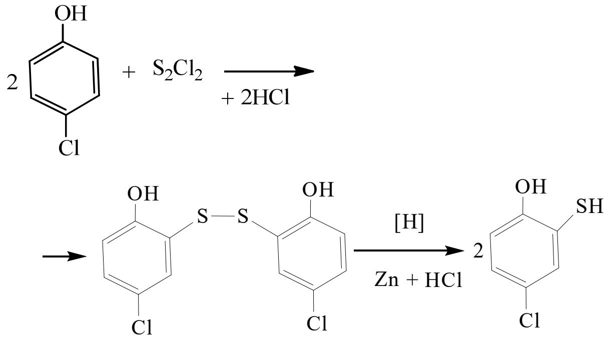
$$D = \frac{[W]_{org}}{[W]_{aq}} \qquad (1)$$

$$R = \frac{100 \times D}{D + \frac{V_{aq}}{V_{org}}} \qquad (2)$$

Chloroform, dichloroethane and chlorobenzene appeared to be the best extractants. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform about 97,8–98,4% of tungsten was extracted as an ion associate. Further researches were conducted with chloroform. The concentration of tungsten in the organic phase was determined with dithiol [19] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

Results and discussion

The synthesis of 2-hydroxy-5-chlorothiophenol is based on the decomposition of phenol disulfide by reduction:

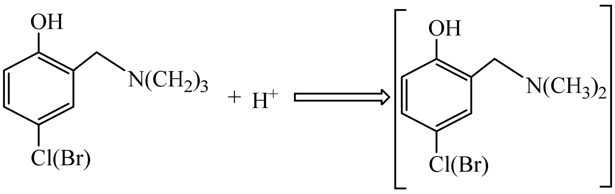


L

2-Hydroxy-5-chlorothiophenol as a dibasic (H_2L) weak acid, depending on the pH of the environment, can be in molecular (H_2L) and anionic forms (HL^-, L^{2-}): pK_1 = 5,10; pK_2 = 10,6 and the pH of the existence of the neutral form is 0,4–3,5 (λ= 283 nm).

Studies on the oxidation state of tungsten. In acidic medium, H_2L exhibit reducing properties [29, 37, 38]. Hence, in the complex formation with H_2L, W (VI) is reduced to W (V) by the reagent itself. This fact was confirmed by ESR spectrometry [37].

Determination of the charge sign of the complexes. The present study is concerned with the investigation of W (V) interaction with H_2L, resulting in the formation of colored complexes insoluble in nonpolar solvents. To determine the sign of the complex charge, ion exchange chromatography was used: AV-17 anion exchanger in chloroform absorbs a part of solution; the chromatographic column is colored in orange, and tungsten is not detected in the filtrate. The anion complex is extracted in the presence of a hydrophobic amine, wherein the complex stability increases, and the color becomes more saturated. To neutralize the charge of the anion complex, aminophenol is used as a hydrophobic amine, which transforms into a aminophenol ion in acidic medium that is:



($AP^{1,2}$) ($AP^{1,2}H^+$)

Influence of aqueous phase pH. The study of the dependence of complexation on pH showed that the yield of W(V)- L -$AP^{1,2}$ is maximum at pH 4.1-5.2. The optimum acidity range for the W(V)-L-AP_1 (1) and W(V)-L-AP_2 (2) complexes is at $pH_{opt.}$ 4.3-5.2 ($pH_{form.}$ 2.2-6.9) and $pH_{opt.}$ 4.1-5.0 ($pH_{form.}$ 2.0-6.8), respectively (Fig. 1, Table 1).

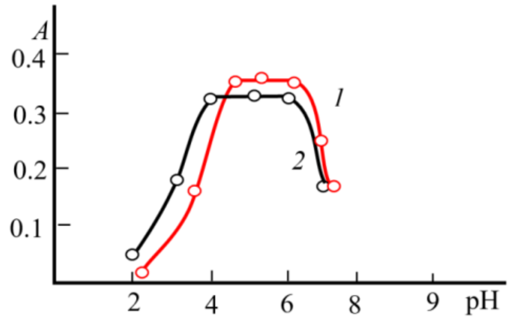


Fig. 1. Influence of aqueous phase pH= 1 (*1*), 2 (*2*): $C_{W(V)}$ = 1,09·10^{-5} mol/l, C_L=1,2·10^{-3} mol/l, C_{AP} = 2.0·10^{-3} mol/l, KFK-2, l = 0,5 cm

Absorption spectra. Tungsten complexes 1 and 2 have maximum absorption at 480 nm and 476 nm, respectively (Fig. 2). While ligand L has maximum absorption at 283 nm. Bathochromic shifts are calculated by the formula $\Delta = \lambda_{W(V)-L} - \lambda_L$ and are 197 nm for 1 and 193 nm for 2. Contrast of reactions was high i.e. initial reagents are colourless while complexes are intensively painted. The molar absorption coefficients are ε_{480} = 2,0·10^4 for 1 and ε_{476} = 2,8·10^4 for 2.

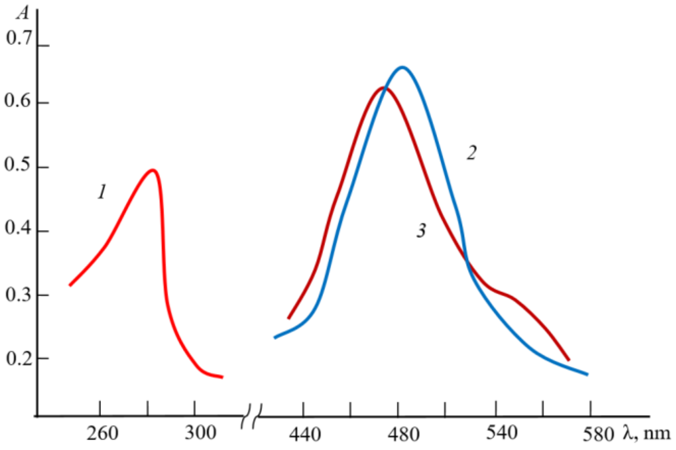


Fig. 2. Electronic spectra of the ligand and W(V)-L-AP^{1,2}complexes: (*1*) L, (*2*) 1, (*3*) 2.
$C_{W(V)} = 1.09\times10^{-5}$M, C_L=1.2×10^{-3}M, $C_{AP} = 2.0\times10^{-3}$M, SF-26.

Reagent concentration and holding time. The effect of L concentration on the completeness of complexation was studied at an optimal pH value and a constant concentration of tungsten and AP^{1,2}. The optimal amount of AP$^{\mathbf{1,2}}$ for maximum binding of the anionic hydroxyl thiophenolate complex of tungsten [W(V)–L] in the mixed ligand complex (MLC) was determined by varying the amount of added AP$^{\mathbf{1,2}}$. The formation of MLC W(V)-L-AP^{1,2} requires a concentration of $1{,}2\cdot10^{-3}$ mol/l H_2L and $2{,}0\cdot10^{-3}$ mol/l AP$^{\mathbf{1,2}}$ in solution. MLC W(V)–L–AP$^{\mathbf{1,2}}$ were stable in aqueous and organic solvents and did not decompose for three days, and after extraction – for more than a month. Maximum absorption was achieved within 5–8 minutes. Phase volume ratios of 5:5 – 115:5 did not affect the recovery. This allows for simultaneous concentration and extraction-spectrophotometric determination of W(V).

Compliance with the fundamental law of light absorption is achieved at $C_{W(V)}$= 0,10–18 μg/ml (Fig. 3). The equations of calibration graphs were calculated: $y = 0{,}273x + 0{,}041$ (for the complex 1) and $y = 0{,}291x + 0{,}048$ (for the complex 2), respectively. Some analytical characteristics of W(V)–L–AP$^{\mathbf{1,2}}$ complexes are given in Table 1.

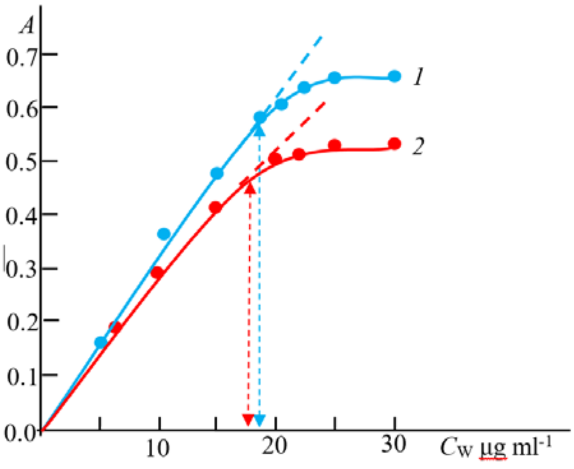


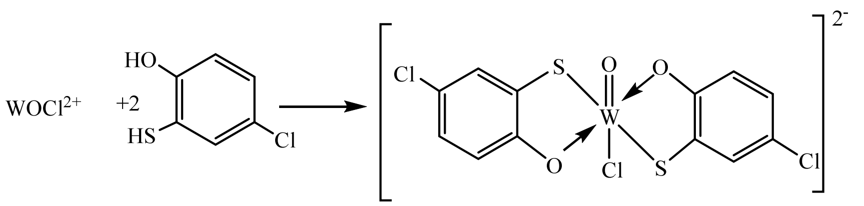
Fig.3. Calibration graph: (*1*) 1, (*2*) 2.

Stoichiometry of the complexes and the mechanism of complexation. The stoichiometry (W^{5+} :L:AP^{1,2} = 1:2:2) of the complexes was determined using the equilibrium shift and Asmus straight line methods [39].

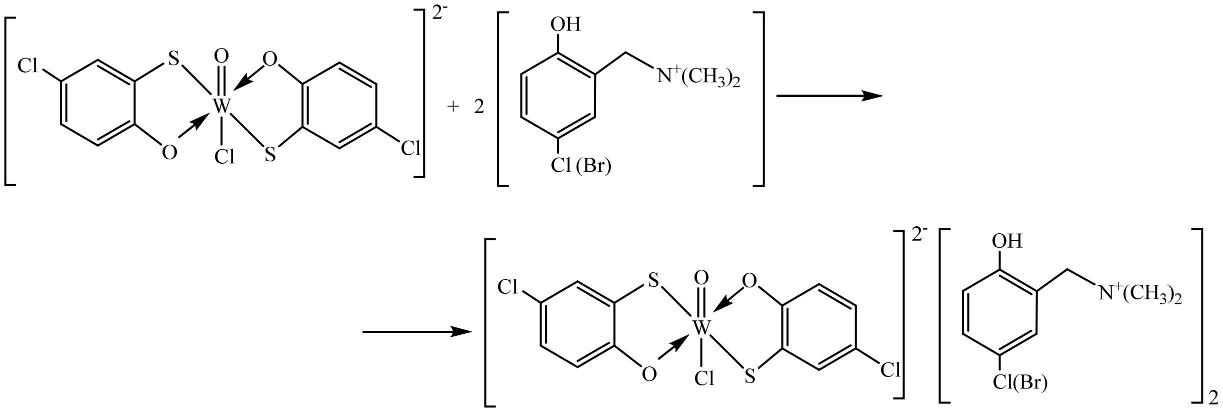
When forming complexes, the coordinating ion is the W^{5+}. The number of protons displaced from one H_2L molecule is 1. $[WOClL_2](AP^{1,2}H)_2$does not polymerize in chloroform (γ = 0,95–1,09).

The stability constant determined by crossed lines method. The stability constant of the complexes at room temperature was calculated: it turned out to be equal to lgβ = 11,97 (for complex 1) and lgβ = 11.25 (for complex 2).The IR spectra of the complexes $[WOClL_2](AP_1H)_2$, in the field of 780–810 cm^{-1}, there is an intensive strip of absorption caused by valent vibration of group $[O{=}W{-}Cl]^{2+}$ [29]. The disappearance of a distinct strip at 2580 sm^{-1}, observed in ranges H_2L and shows that sulfhydryl groups participates in formation of a complex. Observed reduction of intensity of a strip of absorption in area of 3200–3600 sm^{-1}, with a maximum at 3455 sm^{-1}, emergence of a wide strip in area 3050–3150 sm^{-1} shows that the hydroxyl group takes part in formation of coordination communication in the ionized state. Detection of strips of absorption at 2385 cm^{-1} indicates availability of the protonated AP^1 [40].

In a highly acidic medium, there are various cationic forms of W (V) in the solution, with dominating WO^{3+} ion. In hydrochloric acid solutions, this ion can react with Cl^- to form complexes and $WOCl^{2+}$, similarly to molybdenum [37]. The number of protons replaced by tungsten in one H_2L molecule appeared to be two. Given the found component ratio in the complex and an ionic state of tungsten, it was assumed that upon complexation, the following reactions proceed:



(1)



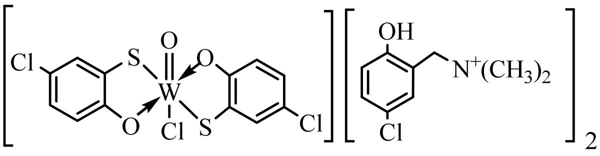
(2)

Table 1.

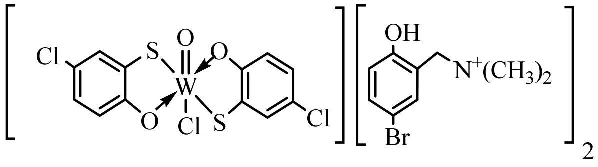
Analytical characteristics of $[WOClL_2](AP^{1,2}H)_2$ complexes

Parameter		1	2
pH	Formation	2,2–6,9	2,0–6,8
	Optim.	4,3–5,2	4,1–5,0
R, %		98,4	97,8
λ, nm		480	476
$\varepsilon \cdot 10^{-4}$		2,4	2,3
γ		1,05	1,06
lgK_{eq}		9,82	10,17
lg_{Kex}		13,78	14,12
lgβ		11,97	11,25
Beer's law execution interval, μg/5 ml		0,5–90	0,5–85
y=a*x*+b		0,273*x* + 0,041	0,291*x* + 0,048
Sandell's sensitivity, μg cm^{-2}		0,0033	0,0034
Limit of detection, ng ml^{-1}		11	12
Limit of quantificat ion, ng ml^{-1}		36	40
Correlation coefficient		0,9987	0,9974

From Eqs (1) and (2), one can judge the reaction mechanism: W (VI) is reduced by H_2L in a HCl medium to W (V), and the latter in the form of a chloride complex cation interacts with excess H_2L. The resulting anionic complex $[WOClL_2]^{2-}$ is reacted with AP, which the acidic solution is in the protonated state (APH^+). The composition of the complexes can be represented by the formula $[WOClL_2](AP^{1,2}H)_2$:



1



2

Thermogravimetric study of $[WOClL_2]$ $(AP^{1,2}H)_2$ complexes showed that thermal decomposition of the complex occurs in three stages: at 60–120°C water evaporates (weight loss 3,75% for 1, 3,16 for 2), at 340–390°C Am decomposes (weight loss 38,66% for 2, 39,43), and at 490–510°C – L (weight loss 33,04% for 1, 39,03 for 2). The final product of thermolysis of the complex is WO_3.

Extraction and equilibrium constants. The complexation reaction can be predicted as follows:

$$W^{5+} + 2H_2L + 2APH^+ \Leftrightarrow [WL_2](APH)_2 + 2H^+ \quad (3)$$

Equilibrium constant (K_{eq}) of the reaction:

$$K_{eq} = \frac{\{[WL_2](APH)_2[H^+]^2\}_{org}}{\{[W^{5+}]\}_{aq}\{[HL]^2\}_{aq}\{[APH^+]^2\}_{aq}}, \quad (4)$$

$$K_{eq} = \frac{\{[WL_2](APH)_2[H^+]^2\}_{org}}{\{[W^{5+}]\}_{aq}\{[HL]^2\}_{aq}} = \lg\frac{A_x}{A_o - A_x}, \quad (5)$$

$$K_{eq} = \frac{D}{[APH^+]^2}, \quad (6)$$

where, A_x – is the optical density for a given experiment; A_o – is the optical density for complete binding of the cobalt ion into a complex.

Taking the logarithm of equation (6), we obtain

$$\lg K_{eq} = \lg D - 2\lg[APH^+] \quad (7)$$

The value of the extraction constant (K_{ex}) can be calculated from equation (8):

$$K_{ex} = \frac{\{[WL_2](APH)_2\}_{org}}{\{[W^{5+}]\}_{org}\{[HL]^2\}_{org}\{[APH^+]^2\}_{org}} = \frac{D}{\{[HL]^2\}_{org}\{[APH^+]^2\}_{org}} \quad (8)$$

$$K_{ex} = \frac{D}{\{[HL]^2\}_{org}\{[APH^+]^2\}_{org}} \quad (9)$$

Taking the logarithm of expression (9), we obtain

$$\lg K_{ex} = \lg D - 2\lg[HL] - 2\lg[APH] \quad (10)$$

The values of K_{eq} and K_{ex}, calculated using formulas (7) and (10), respectively, are given in Table 1.

Influence of foreign ions. It is determined that large amounts of alkali, alkaline earths, and rare earth metals and fluorides, chlorides, and sulfates do not interfere with the determination of tungsten. The interfering effect of Fe (III) was eliminated by introducing a 20% solution of $SnCl_2$ before the addition of the reagent; the effect of Ti (IV) was removed by adding ascorbic acid, and Cu (II), by thiourea. Mo (VI) is acidic medium is reduced with H_2L to Mo (V), which is masked by the addition of EDTA. Because tungsten forms a complex in a more acidic medium than vanadium, tungsten can be determined the presence of large amounts (50 μg) of vanadium.

The proposed method compares favourably with the existing ones (Table 2) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [19–24].

Table 2.

Comparative characteristics of tungsten determination methods

Reagents	pH	λ, nm	ε, 10^{-4}	Reference
Toluene-3,4-dithiol	1,5–2,0	640	1,92	19,24
8-Mercaptoquinoline	0,5–3,0	412	0,367	19,24
8-Hydroxyquinoline	4,4	363	0,64	19,24
KSCN	10 mol/l HCl	405	1,51	19,24
CHPB*	0,49–1,39	420	3,125	23
HPMPPB*	1,0	430	2,2	20
H_2L -AP_1	4,3–5,2	480	2,8	This work
H_2L -AP_2	4,1–5,0	476	2,4	This work

*CHPB – 6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran, HPMPPB – 3-hydroxy-2-[1′-phenyl-3′-(p-methylphenyl)-4′-pyrazolyl]-4-oxo-4H-1-benzopyran.

Analytical applications

Determination of tungsten in steels. 0,1 g weighed sample of steel [composition steel EU-45, %: 0,24 C, 0,60 Mn, 0,03 Si, 3,30 Cr, 0,50 Ni, 0,50 W, 0,50 Mo, 0,30 V, and the rest of Fe] was dissolved under heating in 4 ml of freshly prepared mixture of HCl and HNO_3 (3: 1) in the presence of a few drops of HF. After dissolution, 0,5 ml of HCOOH is added, and the mixture is heated until the decomposition of HNO_3 occurs. After cooling, the mixture is transferred to a 50 ml volumetric flask and diluted up to the mark with water. An aliquot portion of the resulting solution is transferred to a separatory funnel; 3,0 mL of 0,01 mol/l HCl and 0,3–0,5 ml of a 0,01 mol/l H_2L solution were added, and, after thorough mixing, 2,0–3,0 ml of a 0,01 mol/l $AP^{1,2}$ solution was added. The volume of the organic phase was adjusted to 5 ml with chloroform, and the volume of the aqueous phase was brought to 20 ml with distilled water. The mixture is shaken for 5–8 min. After layering of the phases, the absorbance of extracts is measured using a KFK-2 photocolorimeter at 490 nm in cuvettes of 0,5 cm in thickness. The tungsten concentration is found from the calibration curve. The results of the determination of tungsten in steel demonstrate the reliability of the proposed procedure (Table 3).

Table 3.

Tungsten content in steel and samples soil determined by different methods (*n*=5, *P*=95%)

Analyzed object	Method	Found in sample, %	$\overline{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$	S_r
Tungsten content in steel (EU-45: 0,50 % W)	Toluene-3,4-dithiol	0,50	0,50 ±0,138	0,022
	8-Mercaptoquinoline	0,52	0,52 ±0,119	0,025
	8-Hydroxyquinoline	0,49	0,49±0,210	0,017
	H_2L–AP_1	0,51	0,51±0,112	0,019
	H_2L–AP_2	0,48	0,48±0,110	0,012
Tungsten content in soil ($X\cdot10^4$, %)	Toluene-3,4-dithiol	4,65	$(4,65\cdot10^4) \pm 0,064$	0,039
	8-Mercaptoquinoline	4,53	$(4,53\cdot10^4) \pm 0,057$	0,033
	8-Hydroxyquinoline	4,92	$(4,92\cdot10^4) \pm 0,038$	0,024
	H_2L–AP_1	4,85	$(4,85\cdot10^4) \pm 0,026$	0,026
	H_2L–AP_2	4,49	$(4,49\cdot10^4) \pm 0,037$	0,019

Determination of tungsten in soils. The proposed procedures for the determination of tungsten were applied to its determination in light-chestnut soil from the Caspian zone. A 0,5 g weight was finely ground in an agate mortar and calcined in muffle furnace for 3 h. After cooling, the sample was treated and dissolved in a graphite cup in a mixture of 16 ml of HF (conc.), 5 ml of HNO_3

(conc.), and 15 ml of HCl (conc.) at 50–60ºC to remove excess hydrogen fluoride. A further 8 ml portion of HNO_3 (conc.) was added triply to the solution that was each time evaporated to 5-6 ml. After that, the solution was transferred into a 100 ml volumetric flask and its volume was brought to the mark with distilled water. Tungsten was determined in aliquot portions of the solution using the proposed procedures. The accuracy of the results was checked by three independent methods. The results are listed in (Table 3).

Conclusion

MLC of W (V) with H_2L and $AP^{1,2}$ have been studied by spectrophotometry. Extraction of MLC is maximal at pH 4,1–5,2. The optimal conditions for the formation and extraction of MLC have been found. The molar ratio of the reacting W(V), H_2L and $AP^{1,2}$ species is 1:2:2. The general formula of the MLC is $[WOClL_2](AP^{1,2}H)_2$. They can be regarded as ion-associates between doubly charged anionic chelates $[WOClL_2]^{2-}$ and protonated $AP^{1,2}$ species. The developed method retains specific interaction of W (V) with H_2L and $AP^{1,2}$ to form a colored complex and has good sensitivity. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity and sensitivity. Hence, in the complex formation with H_2L, W (VI) is reduced to W (V) by the reagent itself. This fact was also confirmed by ESR spectrometry. $CHCl_3$, CCl_4, $C_2H_2Cl_2$, C_6H_6, C_6H_5-CH_3, *iso*-C_4H_9OH, *iso*-$C_5H_{11}OH$, *n*-C_4H_9OH and their mixtures were tested as extractants. $CHCl_3$ demonstrated the best result; it was used in further experiments. Beer's law is obeyed over the concentration range 0,10–18 µg ml^{-1} W(V). The proposed method were applied to the determination of tungsten in steel and samples of soil.

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Конфликт интересов

Авторы заявляют об отсутствии конфликта интересов

Поступила 9 января 2025 г; принята к публикации 27 февраля 2025 г.

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Conflicts of interests

The authors declare no conflicts of interests.

Submitted 9 January 2025; accepted 27 February 2025